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XVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-
POUNDS.

FIFTH PAPER.

PARACHLORBENZYL COMPOUNDS.

BY C. LORING JACKSON AND J. FLEMING WHITE.

Presented March 12, 1879.

IN the fourth paper of this series the necessity of a revision of all the so-called parachlorbenzyl compounds was pointed out, and the results were described, which had been obtained from the investigation of some of them by Mr. A. W. Field and one of us. This work is now finished, and we have the honor of laying before the Academy a description of the preparation and properties of the remaining parachlorbenzyl compounds, which have been heretofore made in an impure state, and also of a few related substances not as yet described.

Parachlorbenzylbromide melting-point, $48\frac{1}{2}^{\circ}$ (made from pure paratoluidine), was used as the starting-point for these compounds, and therefore they cannot contain the isomeric impurities which caused the mistakes of our predecessors.

A comparison, in tabular form, of our more important results with the earlier ones, will be found at the end of the paper.

Parachlorbenzylsulphoacid, $C_6H_4ClCH_2SO_3H$.

This substance was first studied by Böhler,* whose paper, published in 1869, contains a description of the preparation of the potassium salt by heating chlorbenzylchloride with neutral potassic sulphite. It was, in fact, one of the papers coming from Strecker's laboratory to illustrate his general method of making sulphoacids,† first announced

* Böhler, Ann. Chem. Pharm. 154, p. 56.

† Strecker, Ann. Chem. Pharm. 148, p. 90.

in 1868. The salt was thus obtained in colorless needles which gave with baric chloride glistening crystals of $(C_7H_6ClSO_3)_2Ba \cdot H_2O$; the acid (made from the barium salt with sulphuric acid) formed when heated with an excess of plumbic hydrate, a basic lead salt, $(C_7H_6ClSO_3)_2Pb \cdot PbO_2H_2$, crystallized in scales with a silvery lustre; while with less plumbic hydrate a neutral salt was obtained, which, however, he did not analyze. All these salts were made from ordinary chlorbenzylchloride, and must therefore have been contaminated with the corresponding ortho compounds, as indeed was proved by Vogt and Henninger,* who took up the subject again in 1872, and by fusing the potassium salt (made according to Böhler's method) with potassic hydrate obtained a mixture of salicylic and paraoxybenzoic acids. They did not try, however, to separate the para from the ortho compound, but contented themselves with analyzing Böhler's potassium and barium salts: for the first they found the formula $C_7H_6ClSO_3K \cdot H_2O$; it crystallized from water in concentric groups of large flat needles, from alcohol in pearly plates, lost its water of crystallization at 160° , and was decomposed at higher temperatures; their barium salt agreed in amount of water of crystallization and properties with that of Böhler, except that it crystallized in bunches of needles. In preparing their potassium salt Vogt and Henninger observed the formation of an insoluble substance which, purified by crystallization from alcohol, melted at 167° and had the formula $(C_7H_6Cl)_2SO_2$; from the mother-liquors small quantities of two other substances were obtained, melting at 149° and 185° , and apparently having the same composition; they supposed, therefore, that the main product (melting-point 167°) was a mixture of these, and called it chlorinated benzylosulphide, — a name which, according to our present nomenclature, would be altered to dichlorbenzylsulphone. For a revision of their work on this substance, see page 314.

In taking up the subject we followed the method of our predecessors, except that we used sodic instead of potassic sulphite,† which we made by saturating one half of a strong solution of sodic carbonate with sulphurous dioxide, and then adding to it the other half. After boiling this solution with parachlorbenzylbromide, in the proportion of one molecule of bromide to one of sulphite, in a flask with a return-cooler for seven hours, the smell of the benzylbromide had disappeared; the liquid was therefore allowed to cool, and the insol-

* Vogt and Henninger, *Ann. Chem. Pharm.* 165, p. 372.

† Potassic sulphite is to be preferred, however. See p. 309.

uble portion removed by filtration. This should have been the sulphone described by Vogt and Henninger, but it melted at about 55° instead of 167° , and a qualitative test showed that it contained no sulphur; from the smell it seemed to be an impure parachlorbenzyl-alcohol, formed by the action of the water on the bromide, and it was not thought worth while to investigate it farther. Although we have repeated the preparation of the sodium salt many times, we have never observed the formation of Vogt and Henninger's sulphone, but have got invariably this substance with a much lower melting-point.

The *Sodium Salt*, $C_6H_4ClCH_2SO_3Na$, was purified by evaporating the filtrate from the insoluble substance just described to dryness, boiling the residue with absolute alcohol to remove the organic salt from the sodic bromide, and finally recrystallizing* from a very little water by spontaneous evaporation.

1.8405 grs. of the salt dried in vacuo lost when heated to 160° 0.005 gr., corresponding to 0.27 per cent.

0.4160 gr. lost at 160° 0.002 gr., corresponding to 0.48 per cent.

As one molecule of water corresponds to 7.30 per cent, it is evident that the salt crystallizes without water, and the slight loss observed is due to a partial decomposition of the substance. This view is confirmed by the fact that the 1.8405 grs. used in the first experiment lost only 1 mgr. when the temperature was not allowed to go above 100° .

0.5650 gr. of the salt dried at 160° gave by the method of Carius 0.3512 gr. AgCl and 0.5804 gr. $BaSO_4$.

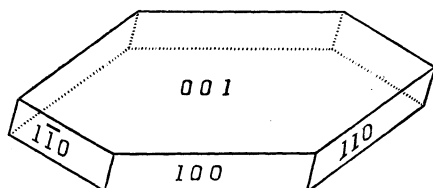
	Calculated for $C_7H_6ClSO_3Na$.	Found.
Chlorine	15.54	15.37
Sulphur	14.00	14.11

Crystallized from water it forms large flat colorless crystals with pointed ends; from alcohol, pearly scales; it is freely soluble in water, but only sparingly in alcohol.

Dr. F. A. Gooch, who has had the kindness to examine the substance crystallographically for us, reports that "the crystals did not admit of measurement with the goniometer; but an examination of some of the smaller ones, under the microscope, between crossed Nicols, proved them to be triclinic (see figure); the planes of polarization of the Nicols making, in the case of a crystal lying upon its basal plane angles of about 5° and 175° , or 85° and 95° respectively with the edge 100—001, when the plane of polarization of the ray from

the polarizer remains unchanged. The apparent angles of the adjacent edges, when the crystal lies upon its basal plane, are approximately as follows:—

Edge 100—001 upon edge 110—001	141°
“ 100—001 “ “ 1 $\bar{1}$ 0—001	147°
“ 110—001 “ “ 1 $\bar{1}$ 0—001	72°



The *Potassium Salt*, $C_6H_4ClCH_2SO_3K$, was made by adding potassic sulphate to the barium salt; the filtrate from the baric sulphate formed was evaporated to dryness, and the organic salt, dissolved out from the excess of potassic sulphate with absolute alcohol, purified by crystallization from water.

1.1328 grs. of the salt dried in vacuo lost when heated to 160° 0.0075 gr., corresponding to 0.66 per cent.

As one molecule of water corresponds to 6.85' per cent, it is evident that this salt, like that of sodium, is free from water of crystallization.

0.3000 gr. of the salt dried at 160° gave by the method of Carius 0.1760 gr. $AgCl$.

0.3165 gr. gave by the same method 0.3025 gr. $BaSO_4$.

0.3065 gr. gave, when heated with pure H_2SO_4 , 0.1075 gr. of K_2SO_4 .

	Calculated for $C_6H_4ClSO_3K$.	Found.
Chlorine	14.50	14.50
Sulphur	13.08	13.13
Potassium	15.98	15.75

It resembles the sodium salt closely in appearance, but is much more soluble in alcohol. As, therefore, the separation of this salt from potassic bromide would be easier than that of the corresponding sodium compounds, it is better in making a salt of the sulphoacid from parachlorbenzylbromide to use potassic in place of sodic sulphite.

To prepare the other salts of the parachlorbenzylsulphoacid the mother-liquor of the sodium salt was treated with a small quantity

of a solution of plumbic acetate, which precipitated plumbic bromide and sulphite; after these had been removed by filtration an excess of plumbic acetate threw down the lead salt of the sulphoacid, which was purified by recrystallization from water, and then decomposed with sulphuretted hydrogen; the filtrate from the plumbic sulphide was concentrated by evaporation, and the solution of parachlorobenzylsulphoacid thus obtained used in the preparation of the following salts.

The *Barium Salt*, $(C_6H_4ClCH_2SO_3)_2Ba \cdot 2H_2O$, was made by boiling the acid with pure baric carbonate. It can also be prepared by the addition of baric chloride to the sodium salt, but in this case it was found hard to free it from the excess of baric chloride.

0.9290 gr. of the salt dried in vacuo lost when heated to 160° 0.0565 gr.

0.5408 gr. lost 0.0332 gr.

	Calculated for $(C_7H_6ClSO_3)_2Ba \cdot 2H_2O$	Found.	
Water	6.16	6.08	6.12

0.1575 gr. of the salt dried at 160° gave, after precipitation with dilute H_2SO_4 , 0.0680 gr. of $BaSO_4$.

0.4620 gr. gave 0.1995 gr. $BaSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Ba$.	Found.	
Barium	25.00	25.38	25.39

It crystallizes from water in radiated bunches of white needles which are moderately soluble in water.

The *Calcium Salt*, $(C_6H_4ClCH_2SO_3)_2Ca \cdot 7H_2O$, was made by warming the aqueous solution of the acid with calcic carbonate, filtering and allowing the concentrated filtrate to evaporate spontaneously; it was purified by recrystallization from water.

0.5805 gr. of the air-dried salt lost in vacuo 0.1033 gr.; when heated to 160° , 0.0332 gr.; making in all 0.1365 gr.

0.9536 gr. lost in vacuo 0.1506 gr.; when heated to 160° , 0.0552 gr.; making in all 0.2058 gr.

	Calculated for $(C_7H_6ClSO_3)_2Ca \cdot 7H_2O$.	Found.	
Water	21.84	23.51	21.58

	Calculated for $(C_7H_6ClSO_3)_2Ca \cdot 2H_2O$.	Found.	
Water	7.39	6.96	6.87

The air-dried salt, therefore, contains seven molecules of water of crystallization, five of which it gives up in vacuo, while a heat of 160° is necessary to remove the whole of its water. The very high result of the first water determination was undoubtedly due to hygroscopic moisture in the air-dried salt.

0.6976 gr. of the salt dried at 160° gave, after precipitation with ammoniac oxalate and ignition over the blast-lamp, 0.085 gr. of CaO.

	Calculated for $(C_7H_6ClSO_3)_2Ca$.	Found.
Calcium	8.87	8.70

It forms rhombic crystals so nearly square that they look like flattened cubes, freely soluble in water.

The *Copper Salt*, $(C_6H_4ClCH_2SO_3)_2Cu \cdot 2H_2O$, was made by warming the aqueous solution of the acid with pure cupric carbonate, and concentrating the filtrate on the water-bath; the crystals thus obtained were recrystallized from water.

0.7400 gr. of the salt dried in vacuo lost when heated to 160° 0.0525 gr.

	Calculated for $(C_7H_6ClSO_3)_2Cu \cdot 2H_2O$.	Found.
Water	7.08	7.05

0.5000 gr. of the salt dried at 160° gave by precipitation with sodic hydrate 0.0833 gr. of CuO.

	Calculated for $(C_7H_6ClSO_3)_2Cu$.	Found.
Copper	13.37	13.30

It crystallizes in pale green needles grouped in bundles, and is readily soluble in water.

The neutral *Lead Salt*, $(C_6H_4ClCH_2SO_3)_2Pb \cdot H_2O$, was made by treating an aqueous solution of the acid with plumbic hydrate not in excess, the solution was evaporated in vacuo, and the crystals washed with a little water to free them from the acid. It is probable from the resemblance in crystalline form, that the precipitate formed on adding a strong solution of the sodium salt to plumbic acetate consists of this salt.

0.8695 gr. of the salt dried in vacuo lost when heated to 100° 0.0261 gr.

0.1910 gr. lost at 100° 0.0056 gr.

0.1900 gr. of the salt dried in vacuo gave, after precipitation with dilute H_2SO_4 , 0.0902 gr. of $PbSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb \cdot H_2O$.	Found.	
Water	2.83	3.00	2.93
Lead	32.55	32.43	

0.1742 gr. of the salt dried at 100° gave 0.0850 gr. of $PbSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb$.	Found.
Lead	33.50	33.34

It crystallizes in long white needles grouped in sheaves or stars, which are not freely soluble in water.

Two *Basic Lead Salts* were obtained by treating the mother-liquor from the preceding salt with an excess of plumbic hydrate; one crystallized from water by spontaneous evaporation in little spheres made up of radiating needles, and seemed to be free from water of crystallization, although it blackened and lost weight at 160° .

0.3384 gr. of the salt dried at 100° gave, after precipitation with dilute H_2SO_4 , 0.2890 gr. of $PbSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb_3O_2$.	Found.
Lead	58.35	58.34

The formula of this salt is therefore $(C_6H_4ClCH_2SO_3)_2Pb_3O_2$. The second salt which crystallized from a hot concentrated solution in white scales had the formula $C_6H_4ClCH_2SO_3PbOH \cdot H_2O$.

0.2128 gr. of the salt dried in vacuo lost at 120° 0.0087 gr.

0.2747 gr. of the salt dried in vacuo gave with dilute H_2SO_4 0.1870 gr. $PbSO_4$.

	Calculated for $C_7H_6ClSO_3PbOH \cdot H_2O$.	Found.
Water	4.02	4.08
Lead	46.26	46.49

To obtain the *Free Acid* the lead salt, which had been purified with great care, was suspended in water, and decomposed with sulphuretted hydrogen, the filtrate from the plumbic sulphide formed was evaporated in a stream of sulphuretted hydrogen, first on the water-bath, and finally at a still lower temperature, until it had attained the consistency of syrup; it was then put in vacuo, where after standing some time it crystallized in square plates, which, however, soon turned yellow, while fumes were given off which smelt of hydrochloric acid and benzaldehyd. These yellow crystals melted at 108° , but the evidences of decomposition were so marked that we do not consider this the true melting-point of the acid, nor did it seem worth

while at present to follow the investigation of such an unstable substance farther.

The *Chloride*, $C_6H_4ClCH_2SO_2Cl$, was made by grinding the dry sodium salt with phosphoric pentachloride, and afterward warming the mixture gently in a porcelain dish on the sand-bath; the oily mass thus obtained gave with water the chloride as a heavy oil, which soon solidified, and was purified by crystallization from ether.

0.1410 gr. of substance gave by the method of Carius 0.1768 gr. of $AgCl$ and 0.1470 gr. of $BaSO_4$.

	Calculated for $C_7H_6ClSO_2Cl$.	Found.
Chlorine	31.55	31.02
Sulphur	14.22	14.32

It forms white flattened crystals, often arranged in indistinct pen-nate groups, and having an aromatic odor; melting-point $85\frac{1}{2}^{\circ}$; it is insoluble in water, soluble in ether and alcohol, but seems to be decomposed by the latter.

Parachlorbenzylsulphide, $(C_6H_4ClCH_2)_2S$.

Pauly* described this substance, which he obtained from chlorbenzylchloride (or bromide), by the action of an alcoholic solution of potassic sulphide, as a thick brown oil, with an unpleasant odor; and adds, that it did not solidify even after standing several days.

On warming an alcoholic solution of parachlorbenzylbromide with sodic sulphide (prepared by saturating one half of an alcoholic solution of $NaOH$ with H_2S , and then adding the other half) we obtained by precipitation of the product with water a heavy oil, which we dissolved in hot alcohol; on cooling this saturated solution a purer oil separated, that solidified on standing over night, and was then purified by recrystallization from hot alcohol.

0.2760 gr. of the substance dried in vacuo gave on combustion 0.5970 gr. of Co_2 and 0.1110 gr. of H_2O .

	Calculated for $(C_7H_6Cl)_2S$.	Found.
Carbon	59.35	59.00
Hydrogen	4.24	4.47

It forms thick white needles, often seven centimeters long, with very little odor; from a hot alcoholic solution, it is sometimes depos-

* Pauly, Ann. Chem. Pharm. 167, p. 187.

ited as an oil, which solidifies by scratching with a sharp glass rod; melting-point, 42° ; it cannot be sublimed without decomposition; essentially insoluble in water, soluble in cold, more freely in hot alcohol, easily soluble in ether, benzole, carbonic disulphide, and glacial acetic acid.

Diparachlorbenzylsulphone, $(C_6H_4ClCH_2)_2SO_2$, was made by adding the calculated amount of chromic anhydride in small quantities at a time to the preceding substance, both bodies being dissolved in glacial acetic acid; the product of the oxidation, washed with water until free from compounds of chromium, was purified by crystallization from alcohol. The substance was also formed by the oxidizing action of the air on parachlorbenzylsulphide.

0.3510 gr. of the substance gave, according to Carius, 0.3195 gr. of AgCl and 0.2610 gr. of $BaSO_4$.

	Calculated for $(C_6H_4Cl)_2SO_2$.	Found.
Chlorine	22.54	22.51
Sulphur	10.16	10.21

It crystallizes in very small needles, melts at 165° , and cannot be sublimed without decomposition; it is essentially insoluble in water, readily soluble in alcohol, ether, carbonic disulphide, glacial acetic acid, and ligroine. The melting-point of this substance (165°) is essentially the same as that of the sulphone (167°), obtained in largest quantity by Vogt and Henninger from the action of chlorbenzylchloride on potassic sulphite, and mentioned on page 307. The isomere, melting at 149° , obtained by them, was probably the corresponding orthochlorbenzylsulphone, but it is hard to understand what the substance melting at 185° could have been. It will be remembered that we did not succeed in obtaining a sulphone when we repeated their work.

Parachlorbenzylmercaptan, $C_6H_4ClCH_2SH$.

The first attempt to prepare this substance was made in 1860 by Beilstein,* who heated a somewhat indefinite mixture of dichlor-substitution products of toluol with potassic sulphhydrate, and obtained an oil which on exposure to the air yielded well-formed octahedra with a vitreous lustre, melting from the first preparation at 77° – 78° , from the second at 84° – 85° . Later, Neuhof† tried the same experiment

* Beilstein, Ann. Chem. Pharm. 116, p. 336.

† Neuhof, Ann. Chem. Pharm. 147, p. 339.

with a mixture of ortho- and parachlorbenzylchloride, and confirmed the results of Beilstein, as the melting-point of his crystals was 84° – 85° . In repeating their work, we found that on mixing alcoholic solutions of parachlorbenzylbromide and KSH (prepared by saturating an alcoholic solution of potassic hydrate with sulphuretted hydrogen), heat was given off, and the action was finished without the aid of external heat in about half an hour; on adding water to the product, a dark-colored oil was precipitated, which, purified by distillation with steam, was frozen by immersion in ice and salt, and recrystallized from alcohol with the aid of a freezing mixture.

0.2560 gr. of the substance dried in vacuo, treated by the method of Carius, gave 0.2276 gr. of AgCl and 0.3750 gr. of BaSO₄.

	Calculated for C_7H_6ClSH .	Found.
Chlorine	22.40	22.00
Sulphur	20.19	20.12

At ordinary temperatures, it is a colorless liquid with a most repulsive and nauseating smell; in a freezing mixture of ice and salt, it solidifies in white crystals, which melt from 19° to 20° . We are not certain that this is the true melting-point of the substance, as a small portion of it may have been converted into the disulphide by the action of the air, and the elementary analysis cannot show the presence of this impurity, but the number here given cannot be very far from the truth, as we got in no case a melting-point much above 20° , and the substance was reduced with zinc and dilute sulphuric acid, so as to convert any disulphide into mercaptan, before taking some of the melting-points. It distils with steam, and mixes readily with alcohol, ether, benzole, and carbonic disulphide, but not with water. Yellow mercuric oxide attacks it with great energy, and converts it into the following compound.

Parachlorbenzylmercaptid, $(C_6H_4ClCH_2S)_2Hg$, was purified by repeated crystallization from boiling alcohol.

0.4820 gr. of the substance dried in vacuo gave by precipitation with H₂S 0.2175 gr. of HgS.

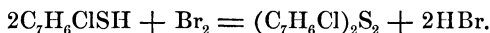
	Calculated for $(C_6H_4ClS)_2Hg$.	Found.
Mercury	38.84	38.91

It forms light white needles without odor, which seem to have no definite melting-point, although the substance turns red or black, and shrinks to about one half of its original volume in the neighborhood

of 160° ; it is insoluble in water, very slightly soluble in ether, benzole, carbonic disulphide, glacial acetic acid, and cold alcohol; more readily, but still not very freely, soluble in hot alcohol. It is decomposed by sulphuretted hydrogen into mercuric sulphide and the mercaptan.

Parachlorbenzylidisulphide, $(C_6H_4ClCH_2)_2S_2$.

This substance was made in several different ways:— (1.) When parachlorbenzylbromide was boiled for two or more days with an alcoholic solution of potassic sulphhydrate, on evaporating off the alcohol a mixture of the oily mercaptan with needles of the disulphide was obtained, which was exposed to the air for some time to oxidize the mercaptan. (2.) The parachlorbenzylmercaptan was treated with the calculated amount of bromine dissolved in ether; the reaction is as follows:—



When a large excess of bromine was added, the product was an oil with an aromatic smell, the study of which is postponed for the present. (3.) Parachlorbenzylbromide was warmed with an alcoholic solution of sodic disulphide (Na_2S_2) obtained by dissolving the calculated amount of flowers of sulphur in an alcoholic solution of sodic sulphide (Na_2S). The products of all these methods had the same melting-point and properties.

For analysis, a specimen prepared according to the first method was purified by crystallization from alcohol and dried in vacuo.

0.3925 gr. of the substance gave on combustion 0.7615 gr. of CO_2 and 0.1475 gr. of H_2O .

0.2540 gr. gave, according to the method of Carius, 0.3780 gr. of $BaSO_4$.

	Calculated for $(C_6H_4Cl)_2S_2$.	Found.
Carbon	53.34	52.91
Hydrogen	3.81	4.17
Sulphur	20.32	20.44

It forms flattened white needles with a disagreeable smell, somewhat like that of the mercaptan, but much less nauseating; melting-point 59° ; insoluble in water, readily soluble in alcohol, glacial acetic acid, and ligroine, very soluble in ether, benzole, and carbonic disulphide. Neither mercuric oxide nor mercuric chloride has any action upon it. Nascent hydrogen made from zinc and dilute sulphuric acid converts it into the mercaptan.

Beilstein, and afterward Neuhof, obtained their so-called mercaptan (melting-point 84° – 85°) by boiling the substances together for a long time, which we find, as already stated, gives the disulphide as principal product; furthermore, their crystals were formed only after long exposure of the liquid product of the reaction to the air. It would seem, therefore, that their substance must have been the disulphide, the percentage composition of which is essentially the same as that of the mercaptan, and therefore the two substances could not be distinguished by analysis, but only by treatment with mercuric oxide, which they do not seem to have tried. On the other hand, the melting-point of their substance (84°) is much higher than that of ours (59°), and it is certainly strange that a mixture of an ortho- and para-compound should melt at a higher temperature than the pure para-compound; they also describe it as crystallizing in vitreous octahedra, while our substance crystallizes even by slow evaporation of a benzole solution in the flattened needles already mentioned.

Parachlorbenzylsulphidedioxide, $(C_6H_4ClCH_2)_2S_2O_2$, was made by adding the necessary amount of chromic anhydride dissolved in glacial acetic acid to a weighed quantity of the disulphide also dissolved in glacial acetic acid; on the addition of water, an oil was deposited, which became solid on standing in the cold, and was purified by crystallization from alcohol.

0.5870 gr. of the substance dried in vacuo gave, by combustion, 1.0390 grs. CO_2 and 0.1838 gr. of H_2O .

	Calculated for $(C_7H_6Cl)_2S_2O_2$.	Found.
Carbon	48.42	48.27
Hydrogen	3.45	3.48

It is a waxy solid, which becomes crystalline after some time; the melting-point of the specimen analyzed was 120° ; it is insoluble in water, readily soluble in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid.

The *Parachlorbenzylether* was made by boiling parachlorbenzylbromide with an alcoholic solution of sodic hydrate; the product was precipitated with water, and the oil purified by distillation with steam. It was a colorless liquid, which distilled over between 215° – 225° , and did not solidify when cooled to -12° . As its properties therefore agreed essentially with those ascribed to it by

Naquet,* who made it as we did, and Neuhoft,† who obtained it from the chlorbenzylacetate and alcoholic potassic hydrate, we did not think it worth while to analyze or study it more carefully.

We have thus brought our revision of the parachlorbenzyl compounds to an end; the only one previously obtained that we have not studied is the amide of the parachloralphantholuylic acid, which we did not succeed in obtaining by the action of potassic cyanide on parachlorbenzylbromide, although Neuhoft made it in this way from the chlorbenzylchloride. It is possible, but not very probable, that this difference between his results and ours is due to the fact that he used the chloride while we used the bromide.

For convenience of comparison, the melting-points of the substances described in this paper, with those given by our predecessors, are collected in the following table, to which is added a comparison between the amounts of water of crystallization in the salts of the parachlorbenzylsulphoacid, in those heretofore described as such, and in the corresponding salts of the benzylsulphoacid.‡

COMPARISON OF MELTING-POINTS.

Formula of Substance.	Correct Melting-point.	Former Melting-point.	Authority for former Melting-point.
$C_6H_4ClCH_2SO_2Cl$	85½°		
$(C_6H_4ClCH_2)_2S$	42°	Oil	Pauly. [ninger.
$(C_6H_4ClCH_2)_2SO_2$	165°	167°	Vogt and Hen-
		{ 77°-78°	Beilstein.
$C_6H_4ClCH_2SH$	19°	{ 84°-85°	Neuhof.
		{ 84°-85°	
$(C_6H_4ClCH_2)_2S_2$	59°	See above.	
$(C_6H_4ClCH_2)_2S_2O_2$	120°		
$C_6H_4ClCH_2OC_2H_5$	Oil	{ Oil	Naquet.
		{ Oil	Neuhof.

* Naquet, Ann. Chem. Pharm., Supp. 2, p. 249.

† Neuhoft, Ann. Chem. Pharm. 147, p. 339.

‡ Böhler, Zeitschrift der Chemie, 1868, p. 440.

COMPARISON OF THE COMPOSITION OF CERTAIN SALTS OF
CHLORBENZYL AND BENZYL SULPHOACIDS.

Name of Salt.	Chlorbenzylsulphoacid.			Benzyl Sulphoacid.
	Para.	Böhler.	Vogt and Henninger.	
Sodium	No H_2O	—	—	—
Potassium	No H_2O	H_2O	H_2O	H_2O
Barium	$2\text{H}_2\text{O}$	H_2O	H_2O	$2\text{H}_2\text{O}$
Calcium	$\left\{ \begin{array}{c} 7\text{H}_2\text{O} \\ \text{or} \\ 2\text{H}_2\text{O} \end{array} \right\}$	—	—	$2\text{H}_2\text{O}$
Copper	$2\text{H}_2\text{O}$	—	—	No good crystals.
Lead	H_2O	—	—	
Basic Lead	$\text{PbO}_2\text{H}_2 \cdot 2\text{H}_2\text{O}$	PbO_2H_2	—	
Basic Lead	2PbO	—	—	